



IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
SUGIURA ET AL. : EXAMINER: J. L. DOTE
SERIAL NO.: 10/644,938 :
FILED: AUGUST 21, 2003 : GROUP ART UNIT: 1756

FOR: TONER FOR DEVELOPING ELECTROSTATIC IMAGE,
DEVELOPER, PROCESS FOR FORMING IMAGE, AND IMAGE
FORMING APPARATUS

DECLARATION UNDER 37 CFR 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes **Hideki Sugiura** who deposes and states:

1. That I am a graduate of Shizuoka University, and received Master degree in Science in the year of 1992.
2. That I have been employed by Ricoh Company Limited for 13 years as a researcher of Analytical Chemistry, i.e., functional materials (1992-1999) and of Developer, i.e., a toner (1999 to the present)..
3. That I am a co-inventor in the above-identified application.
4. That I have read and understood Sugiyama et al. (US 2002/0081510), Matsuda et al. (US 2003/0104297) and Yagi et al. (US 2003/0138717), which have been cited against the claims in the above-identified application.
5. That toners disclosed in the cited references do not satisfy the requirements of the present invention.
6. That the following additional experiment was conducted under my supervision during the period of from October 11, 2005 to December 15, 2005.

Experiment:

Toners were produced in the same manner as described in Example 14 of Sugiyama et al., Preparation Example 2, Toner 13 of Matsuda et al., and Example 1 of Yagi et al., respectively. Thereafter, the resulted toners, respectively referred herein as Toner 14, Toner 13 and Toner 1, were subjected to the nitrogen contents of the toner particles.

<Production of Toner 14>

Preparation of Prepolymer

In a reactor equipped with a condenser, a stirrer and a nitrogen feed pipe, there were charged 724 parts of an ethylene oxide (2 mol) adduct of bisphenol A, 250 parts of isophthalic acid, 24 parts of terephthalic acid and 2 parts of dibutyltin oxide, and the mixture was reacted at 230°C under a normal pressure for 8 hours. The reaction mixture was further reacted at a reduced pressure of 10-15 mmHg for 5 hours, while removing a water. Thereafter, the reaction mixture was cooled to 160°C, and 32 parts of phthalic anhydride were added thereto and the resulting mixture was reacted for 2 hours. The mixture was cooled to 80°C, and then was reacted with 188 parts of isophorone diisocyanate in ethyl acetate for 2 hours, to thereby yield an isocyanate-containing polyester prepolymer having a weight average molecular weight of 12,000.

Preparation of Ketimine

In a reactor equipped with a stirrer and a thermometer, there were charged 30 parts of isophorone diamine and 70 parts of methylethyl ketone, and the mixture was reacted at 50°C for 5 hours to thereby yield a ketimine compound.

Production of Toner

In a vessel equipped with a stirrer and a thermometer, there were charged 371 parts of non-modified polyester, 108 parts of carnauba wax (molecular weight: 2,000, acid value: 3, melting point:

84°C), 22 parts of a charge controlling agent (zinc complex of salicylic acid E-84, manufactured by Orient Kagaku Kogyo K.K.), 930 parts of ethyl acetate. The mixture was heated up to 80°C while stirring, the temperature was kept at 80°C for 5 hours, and then cooled down to 30°C through 1 hour. To the resulting mixture in the vessel there were added 250 parts of copper phthalocyanine blue and 500 parts of ethyl acetate, and the mixture was stirred for 1 hour to thereby obtain a material solution. 1,430 parts of the material solution was charged into a vessel, and the pigment and the wax therein were dispersed by means of a beads mill (ULTRAVISCOMILL, manufactured by Aimex Co., Ltd.) at a feed rate of 1 kg/hr and disc peripheral speed of 6 m/sec. Zirconia beads having a diameter of 0.5 mm were used in an amount of 80% by volume. The dispersion treatment was repeated by passing the material solution three times through the mill. To the resulting material solution, there was added 1,430 parts of a 65% ethyl acetate solution of non-modified polyester and 209 parts of the above-prepared prepolymer. The mixture was dispersed by means of the above beads mill under the same conditions provided that the mixture was passed through the mill only once. To this dispersed mixture, 37 parts of the above-prepared ketimine compound was dissolved, to thereby obtain a toner material dispersion.

In a beaker, there were placed 706 parts of ion-exchanged water, 294 parts of a 10% hydroxyapatite emulsion (SUPERTITE 10, manufactured by Nippon Kagaku Kogyo Co., Ltd.) and 0.2 parts of sodium dodecylbenzene sulfonate, and the mixed solution was heated up to 60°C. While stirring the solution with TK-type homomixer at rotation speed of 12,000 rpm, the above toner material dispersion was added thereto. The stirring was continued for 10 minutes. The resulting dispersion was placed in a flask equipped with a stirrer and a thermometer, and was heated to 98°C to remove the solvent while reacting the prepolymer and the ketimine compound. The resultant was then filtered, washed, dried and air-classified to obtain toner

particles having a volume average particle diameter of 5 μm . With 100 parts of the toner particles, there were mixed 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide by means of HENSCHEL MIXER to thereby yield Toner 14. The urea-modified polyester contained in Toner 14 had a glass transition temperature of 62°C, an acid value of 10 mg KOH and such a molecular weight distribution according to gel permeation weight of 5,000 and that the portion of the urea-modified polyester having a molecular weight of 30,000 or more accounted for 5% by weight thereof. In Toner 14, there were 88% by number of the wax particles which had a dispersion diameter of 0.1-3 μm .

<Production of Toner 13>

Synthesis of Organic Fine Particle Emulsion

In a reaction vessel equipped with a poker and a thermometer, there were charged 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOR RS-30, manufactured by Sanyo Chemical Industries, Ltd.), 83 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate and 1 part of ammonium persulfate, and the mixture was stirred at 400 rpm for 15 minutes to obtain a white emulsion. The thus obtained emulsion was reacted at 75°C for 5 hours. This was mixed with 30 parts of a 1% aqueous solution of ammonium persulfate, and the mixture was aged at 75°C for 5 hours to thereby obtain an aqueous dispersion of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid). The aqueous dispersion, referred as Fine Particle Dispersion hereinafter, was found to have a volume average particle diameter of 0.10 μm as measured with a particle size analyzer LA-920 (manufactured by Horiba Instruments Inc.). A part of the Fine particle Dispersion was dried to isolate the resin component. The glass transition temperature of the resin component was 57°C.

Preparation of Aqueous Phase

990 parts of water, 80 parts of the Fine Particle Dispersion, 40 parts of a 48.5% aqueous solution of sodium dodecyldiphenyl ether disulfonate (ELEMNOR MON-7, manufactured by Sanyo Chemical Industries, Ltd.) and 90 parts of ethyl acetate were mixed and stirred to obtain a milky liquid, which will be hereinafter referred as Aqueous Phase.

Synthesis of Low Molecular Weight Polyester

Into a reaction vessel equipped with a reflux condenser, a stirrer and a nitrogen gas inlet pipe, there were charged 220 parts of 2 mol ethylene oxide adduct of bisphenol A, 561 parts of 3 mol propylene oxide adduct of bisphenol A, 218 parts of terephthalic acid, 48 parts of adipic acid and 2 parts of dibutyltin oxide, and the mixture was reacted at 230°C under a normal pressure for 8 hours. This reaction mixture was further reacted under a reduced pressure of 10-15 mmHg for 5 hours. To the reaction product was added 45 parts trimellitic anhydride. The mixture was reacted at 180°C under a normal pressure for 2 hours to thereby obtain Low Molecular Weight Polyester having a number average molecular weight of 2,500, a weight average molecular weight of 6,700, a glass transition temperature of 43°C and an acid value of 25.

Synthesis of Prepolymer

In a reaction vessel equipped with a reflux condenser, a stirrer and a nitrogen gas inlet pipe, there were charged 682 parts of 2 mol ethylene oxide adduct of bisphenol A, 81 parts of 2 mol propylene oxide adduct of bisphenol A, 283 parts of terephthalic acid, 22 parts of trimellitic anhydride and 2 parts of dibutyltin oxide, and the mixture was reacted at 230°C under a normal pressure for 8 hours. This reaction mixture was further reacted under a reduced pressure of 10-15 mmHg for 5 hours to thereby obtain Intermediate Polyester having a number average molecular weight of 2,100, a weight average molecular weight of 9,500, a glass transition temperature of 55°C, and acid value

of 0.5 and a hydroxyl value of 49.

In a reaction vessel equipped with a reflux condenser, a stirrer and a nitrogen gas inlet pipe, there were charged 411 parts of the Intermediate Polyester, 89 parts of isophorone diisocyanate and 500 parts of ethyl acetate, and the mixture was reacted at 100°C for 5 hours to thereby yield Prepolymer having a free isocyanate content of 1.53% by weight.

Synthesis of Ketimine

In a reaction vessel equipped with a poker and a thermometer, there were charged 170 parts of isophorone diamine and 75 parts of methyl ethyl ketone, and the mixture was reacted at 50°C for 5 hours to thereby yield Ketimine Compound having an amine value of 418.

Synthesis of Master Batch

40 parts of carbon black (REGAL 400R, manufactured by Cabot Co.), 60 parts of a binder resin (polyester resin RS-801, manufactured by Sanyo Chemical Industries, acid value: 10, Mw: 20,000, Tg: 64°C) and 30 parts of water was mixed in a HENSCHER MIXER to obtain an aggregated mixture impregnated with water. The aggregated mixture was kneaded at 130°C for 45 minutes in a two-roll kneader with the surface temperature of the roll set at 130°C, and the kneaded mixture was pulverized into particles having a diameter of 1 mm with a pulverizer to thereby obtain Master Batch.

Preparation of Oil Phase

In a vessel equipped with a poker and a thermometer, there were charged 378 parts of the Low Molecular Weight Polyester, 110 parts of carnauba wax particles (melting point: 82°C, volume average particle diameter: 590 μ m), 22 parts of a charge controlling agent (salicylic acid metal complex E-84, manufactured by Orient Chemical Industries, Ltd.), and 947 parts of ethyl acetate, and the mixture was heated to 80°C while stirring. The mixture was allowed to stand at 80°C for 5 hours and then cooled to 30°C in 1 hour. Then, 500 parts of the Master Batch and 500 parts of ethyl acetate were charged therein and mixed for 1

hour to thereby obtain Material Solution.

1,324 parts of the Material Solution was charged in a vessel and dispersion of the carbon black and the wax was performed by passing through a beads mill (ULTRAVISCOMILL, manufactured by Aimex Co., Ltd.) filled with zirconia beads having a diameter of 0.5 mm by 80 vol. % three times under conditions of a liquid feeding rate of 1 kg/hr and a disk circumferential velocity of 6 m/sec. This was then mixed with 1,324 parts of a 65% ethyl acetate solution of the Low Molecular Weight Polyester. The mixture was once passed through the beads mill under the same conditions as above to thereby obtain Pigment-Wax Dispersion having a solid concentration of 50% (130°C, 30 minutes).

Emulsification-Deformation-Desolvent

648 parts of the Pigment-Wax Dispersion, 154 parts of the Prepolymer and 6.6 parts of the Ketimine Compound were charged in a vessel and mixed by means of TK HOMOMIXER (manufactured by Tokushu Kika Kogyo Co., Ltd.) at 5,000 rpm for 1 minute. This was then mixed with 1,200 parts of the Aqueous Phase by means of TK HOMOMIXER at 13,000 rpm for 20 minutes to thereby obtain Emulsified Slurry.

The thus obtained Emulsified Slurry was charged in a vessel equipped with a poker and a thermometer and disolvented at 30°C for 8 hours and then at 45°C for 4 hours to thereby obtain Dispersion Slurry having a weight average particle diameter of 5.95 μ m and a number average particle diameter of 5.45 μ m.

Washing-Drying

100 parts of the Dispersion Slurry was filtered under a reduced pressure.

(1) The filter cake and 100 parts of ion-exchanged water were mixed using TK HOMOMIXER at 12,000 rpm for 10 minutes, and the mixture was filtered,

(2) The filter cake obtained in (1) and 100 parts of a 10% aqueous solution of sodium hydroxide were mixed using TK HOMOMIXER at

12,000 rpm for 30 minutes under application of ultrasonic vibration. The mixture was then filtered under a reduced pressure. This ultrasonic and alkali washing was repeated once again.

(3) The filter cake obtained in (2) and 100 parts of a 10% hydrochloric acid were mixed using TK HOMOMIXER at 12,000 rpm for 10 minutes. The mixture was then filtered.

(4) The filter cake obtained in (3) and 300 parts of ion-exchanged water were mixed using TK HOMOMIXER at 12,000 rpm for 10 minutes. The mixture was then filtered. This mixing and filtering process was repeated once again to thereby obtain Filter Cake.

The Filter Cake was dried at 45°C for 48 hours in a circulating air drier and then sieved using a 75 μm mesh sieve. 1.0 parts of silica (R974, manufactured by Nippon Aerosil Co., Ltd.) and 0.5 parts of titania (T805, manufactured by Nippon Aerosil Co., Ltd.) were added per 100 parts of the thus obtained particles. After having mixed in a HENSCHEL MIXER, the mixture was passed through a mesh to remove particles having large diameters to thereby obtain Toner 13 having a weight average particle diameter of 6.03 μm and a number average particle diameter of 5.52 μm .

<Production of Toner 1>

Synthesis of Emulsion of Resin Particles

In a reaction container equipped with a stirrer and a thermometer, there were charged 683 parts of water, 11 parts of a sodium salt of sulfate of an adduct of methacrylic acid with ethyleneoxide (EREMINOR RS-30, manufactured by Sanyo Chemical Industries Ltd.), 83 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate, and 1 part of ammonium persulfate, and the mixture was agitated at a revolution of 400 rpm for 15 minutes to thereby obtain a white emulsion. The thus obtained emulsion was heated to 75°C to perform a reaction for 5 hours. Then 30 parts of a 1% aqueous solution of ammoniumpersulfate were added to the emulsion

and the mixture was further aged at 75°C for 5 hours to thereby obtain an aqueous dispersion, referred hereinafter as Particle Dispersion, of a vinyl resin, i.e., a copolymer of styrene-methacrylic acid-butyl methacrylate-a sodium salt of a sulfate of an adduct of methacrylic acid with ethylene oxide. The volume average particle diameter of the Particle Dispersion was 0.10 μm when measured with an instrument LA-920.

A part of the Particle Dispersion was dried to prepare a particulate resin. The glass transition temperature of the particulate resin was 57°C.

Preparation of Aqueous Phase

80 parts of the Particle Dispersion were mixed with 990 parts of water, 40 parts of a 48.5% aqueous solution of sodium dodecyldiphenyletherdisulfonate (EREMINOR MON-7, manufactured by Sanyo Chemical Industries), and 90 parts of ethyl acetate to thereby obtain an Aqueous Phase.

Synthesis of Low Molecular Weight Polyester

In a reaction container equipped with a condenser, a stirrer and a pipe from which a nitrogen gas was supplied to the container, there were charged 220 parts of an adduct of bisphenol A with 2 moles of ethyleneoxide, 561 parts of an adduct of bisphenol A with 3 moles of propylene oxide, 218 parts of terephthalic acid, 48 parts of adipic acid, and 2 parts of dibutyl tin oxide, and the mixture was reacted at 230°C under normal pressure for 8 hours. The reaction was then further performed for 5 hours under a reduced pressure of 10-15 mmHg. 45 parts of trimellitic anhydride were added thereto, and the mixture was reacted at 180°C under a normal pressure for 2 hours to thereby obtain Low Molecular Weight Polyester having a number average molecular weight of 2,500, a weight average molecular weight of 6,700, a glass transition temperature of 43°C, and an acid value of 25.

Preparation of Prepolymer

In a reaction container equipped with a condenser, a stirrer and

a nitrogen gas inlet pipe, there were charged 682 parts of an adduct of bisphenol A with 2 moles of ethylene oxide, 81 parts of an adduct of bisphenol A with 2 moles of propylene oxide, 283 parts of terephthalic acid, 22 parts of trimellitic anhydride, and 2 parts of dibutyl tin oxide. The mixture was reacted at 230°C under a normal pressure for 8 hours, and the reaction was further performed for 5 hours under a reduced pressure of 10-15 mmHg to thereby obtain an intermediate polyester having a number average molecular weight of 2,100, a weight average molecular weight of 9,500, a glass transition temperature of 55°C, an acid value of 0.5 and a hydroxyl value of 49.

In a reaction container equipped with a condenser, a stirrer and a nitrogen gas inlet pipe, there were charged 411 parts of the intermediate polyester, 89 parts of isophoron diisocyanate and 500 parts of ethyl acetate. The mixture was reacted at 100°C for 5 hours to thereby yield Prepolymer having free isocyanate groups in an amount of 1.53% by weight.

Synthesis of Ketimine

In a reaction container equipped with a stirrer and a thermometer, 170 parts of isophorone diamine and 75 parts of methylethyl ketone were mixed. The mixture was reacted at 50°C for 5 hours to thereby obtain Ketimine Compound having an amine value of 418.

Preparation of Master Batch

40 parts of carbon black (REGAL 400R, manufactured by Cabot Corporation), 60 parts of a polyester resin (RS-801, acid value: 10, Mw: 20,000, Tg: 64°C, manufactured by Sanyo Chemical Industries, Ltd) as a binder resin, and 30 parts of water were mixed in a HENSHEL MIXER. Thus, a mixture in which water penetrated into the aggregated pigment was prepared. This mixture was kneaded for 45 hours at 130°C using a two-roll mill. Then the kneaded mixture was pulverized so as to have a particle diameter of 1 mm. Thus, a master batch 1 was prepared.

Preparation of Oil Phase

In a reaction container equipped with a stirrer and a thermometer, there were charged 378 parts of Low Molecular Weight Polyester, 110 parts of carnauba wax, 22 parts of a metal complex of salicylic acid serving as a charge controlling agent (E-84, manufactured by Orient Chemical Industries Co., Ltd.) and 947 parts of ethyl acetate. The mixture was heated at 80°C for 5 hours while agitating and then cooled to 30°C while taking one hour. Then 500 parts of the Master Batch and 500 parts of ethyl acetate were added thereto to be mixed for 1 hour. Thus, a toner constituent solution was prepared.

In a container, 1,324 parts of the toner constituent solution were charged and then dispersed using a beads mill (ULTRAVISCOMILL, manufactured by AIMEX, Co., Ltd.) under the following conditions:

Liquid feeding speed: 1 kg/hr,

Disc rotation speed: 6 m/sec,

Diameter of beads: 0.5 mm,

Filling factor: 80% by volume, and

Repeat number of dispersion treatment: 3 times.

Thus, the carbon black and wax were dispersed. Then 1,324 parts of a 65% ethyl acetate solution of the Low Molecular Weight Polyester were added thereto, and the mixture was dispersed under the conditions mentioned above provided that the repeat number of the dispersion treatment was changed to 1 time to thereby obtain a pigment/wax dispersion. The solid content of the pigment/wax dispersion was 50% when measured by heating the dispersion at 130°C for 30 minutes.

Emulsification and Solvent Removal

In a container, there were charged 648 parts of the pigment/wax dispersion, 154 parts of the Prepolymer and 6.6 parts of the Ketimine Compound, and the mixture was mixed at a revolution of 5,000 rpm for 1 minute by means of a TK HOMOMIXER (manufactured by Tokushu Kikai Kogyo Co., Ltd.). 1,200 parts of the Aqueous Phase were added thereto and the mixture was dispersed at a revolution of 13,000 rpm, for

20 minutes by means of a TK HOMOMIXER to thereby obtain an emulsion slurry.

In a container equipped with a stirrer and a thermometer, the emulsion slurry was added and then was heated at 30°C for 8 hours to remove the solvents therefrom. The slurry was then aged at 45°C for 4 hours to thereby obtain a dispersion slurry. The dispersion slurry had a volume average particle diameter of 5.95 μm , and a number average particle diameter was 5.45 μm when measured by a MULTISIZER II.

Washing and Drying

100 parts of the emulsion slurry were filtered by filtering under a reduced pressure, and then the following operations were performed.

(1) 100 parts of deionized water were added to the thus prepared cake and the mixture was mixed at a revolution of 12,000 rpm for 10 minutes by a TK HOMOMIXER, and then filtered;

(2) 100 parts of a 10% aqueous solution of sodium hydroxide were added to the cake prepared in (1) and the mixture was mixed at a revolution of 12,000 rpm for 30 minutes by a TK HOMOMIXER while applying supersonic vibration thereto, and the filtered under a reduced pressure, wherein this washing using an alkali was repeated twice;

(3) 100 parts of a 10% hydrochloric acid were added to the cake prepared in (2) and the mixture was mixed at a revolution of 12,000 rpm for 10 minutes by a TK HOMOMIXER, and then filtered; and

(4) 300 parts of deionized water were added to the cake prepared in (3) and the mixture was mixed at a revolution of 12,000 rpm for 10 minutes by a TK HOMOMIXER, and then filtered, wherein this washing was repeated twice to thereby obtain a filtered cake.

The thus obtained filtered cake was dried at 45°C for 48 hours using a circulating drier. The dried cake was sieved using a screen having openings of 75 μm to thereby yield Toner 1. Toner 1 had a volume average particle diameter (D_v) of 6.03 μm , and a number average particle diameter (D_n) of 5.52 μm , when measured by a MULTISIZER II. The ratio (D_v/D_n) was 1.09.

Results:

Toner particles of Toner 1, Toner 13, and Toner 14 were subjected to the measurements of nitrogen contents, i.e., a ratio (S/V) of an amount of nitrogen at the surface (S) to an amount of nitrogen in the entire toner particle (V) in the same manner described at pages 19-20 of the present specification.

The results are summarized in the following table.

| Toner | S/V |
|----------|-----|
| Toner 14 | 1.1 |
| Toner 13 | 1.1 |
| Toner 1 | 1.1 |

Conclusion:

As evidenced above, the S/V value of T1, T13 and T14 were all 1.1 which is outside the range of the present invention, 1.2 to 10, and thus the present invention is not anticipated by or obvious over any of the cited references, Sugiura et al., Matsuda et al., and Yagi et al.

7. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

8. Further deponent saith not.

Hideki Sugiura
Hideki Sugiura

December 20, 2005
Date